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WATER-GAS TAR EMULSIONS

BY

W. W. ODELL

THIS PAPER REPRESENTS WORK DONE UNDER A COOPERATIVE AGREEMENT BETWEEN THE BUREAU OF MINES, DEPARTMENT OF THE INTERIOR, THE STATE GEOLOGICAL SURVEY DIVISION OF THE STATE OF ILLINOIS, AND THE ENGINEERING EXPERIMENT STATION OF THE UNIVERSITY OF ILLINOIS

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WATER-GAS TAR EMULSIONS

By W. W. ODELL.

INTRODUCTION.

In numerous water-gas plants throughout the country difficulty has been experienced at various times in separating the tar from the water that is simultaneously condensed from the gas. This difficulty was so serious that the research committee of the Illinois Gas Association suggested it as a problem warranting study and investigation. The suggestion was accepted by the Bureau of Mines and, under the Illinois Cooperative Agreement, the writer made a brief investigation of these tar emulsions. The investigation lasted approximately three months and consisted in the main of a laboratory study of tars and emulsions collected from different plants and produced under different operating conditions.

The purpose of the work was not to find a means of separating tar-water emulsions, but rather to learn more about their formation with the thought in mind that such information might lead the way to a method of operating that would avoid the formation of obstinate emulsions. This paper is chiefly a report of the work done and the conclusions reached.

A laboratory for conducting the necessary tests was furnished by the Peoples Gas Light & Coke Co. at Chicago. This company showed active interest in the work in a number of ways and assigned Mr. E. W. Thiele of its staff of chemists to cooperate and assist in conducting the tests. Mr. Thiele devoted his time entirely to this work during the period mentioned and gave valuable assistance.

ACKNOWLEDGMENTS.

Grateful acknowledgment is here made of the valuable suggestions and encouragement given the writer by A. C. Fieldner, supervising chemist of the Pittsburgh station of the Bureau of Mines, and his staff; by R. B. Harper, chief chemist of the Peoples Gas Light & Coke Co.; Professor Parr, of the University of Illinois; and O. P. Hood, chief mechanical engineer of the Bureau of Mines.

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LABORATORY TESTS.

Chiefly the laboratory work consisted in making the following tests:

(1) Tar distillations.

(2) Sulphonation of tar-distillate fractions.

(3) Distillation of gas oils and sulphonation of the distillate fractions.

(4) Specific gravity determinations of the tars and of the distillate fractions therefrom.

(5) Determination of the percentage of acids in tar-distillate fractions.

(6) Determination of the percentage of free carbon in the tars.

(7) Centrifuge tests. Settling tests.

(8) Determination of sulphur in the tars and gas oils.

(9) Filtration, and miscellaneous minor tests of tars.

(10) Determination of ammonia, sulphur, tar acids, etc., in the water of emulsions, and the making of surface-tension tests.

The distillations were made in a 500-c. c. standard glass distillation flask. Two hundred gram samples were used for both tar and oil distillations. A nitrogen-filled centigrade thermometer was used with the mercury bulb placed at the side-arm offtake. No corrections were made for emergent stem. The same thermometer, in the same position, was used throughout all the tests.

The distillate fractions were sulphonated by adding concentrated sulphuric acid to approximately 10 c. c. of the oil (a weighed quantity) in a cream bottle. The acid was added 10 c. c. at a time, the bottle shaken after each addition, to mix the contents, and after the bottle was filled with the acid it was placed in water at nearly the boiling temperature for one hour and then centrifuged. The oil not sulphonated was thus forced to the top of the bottle, where its volume could be read directly.

The specific gravity determinations were made in a picnometer fitted with a thermometer in all tests where the fractions were large enough. For fractions that were chiefly solid at 60° F., the determination was made at a higher temperature and a correction made for the difference. For each 1° F. above 60° F., 0.0004 was added to the specific gravity value found.

Tar-acid tests were made by treating the fractions with caustic alkali in special separatory funnels, separating the alkaline extract by draining off the oily residue and then liberating the acid from its alkaline compound by adding sulphuric acid and agitating in the same apparatus. The percentage of acid was read from the graduations provided for that purpose.

The percentage of free carbon was not determined by the Soxhlet extraction method, but a gram sample of tar was diluted with a

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mixture of benzol and toluol and the whole was washed through an alundum crucible fitted to a suction flask in which a vacuum was maintained by a water suction pump. Additional solvent was washed through the crucible until it came through colorless. Then the crucible was dried and weighed; the difference between this weight and the original weight was taken as free carbon. The residue from igniting this carbon in the crucible was taken as the ash in the tar.

The centrifuge tests consisted merely in centrifuging samples at different temperatures and with different solvents, in a hand centrifuge at speeds up to 2,000 r. p. m. The samples were put in Babcock bottles—used for the determination of fat in milk and cream—before centrifuging.

The sulphur in the tar and oil was determined by burning a small amount, 0.5 gram or slightly less, in a Parr bomb according to the regular method. The residue after combustion was washed into a beaker, treated in the usual manner, and the sulphur was estimated gravimetrically.

Ammonia in the waters was determined by titration with standard N/10 or N/30 sulphuric acid. The sulphur was determined gravimetrically by precipitation as barium sulphate after treatment with hydrogen perodixe (free from sulphuric acid) and acidification with hydrochloric acid.

WATER-GAS TAR—WHAT IT REALLY IS.

In the manufacture of carbureted water gas the only fuel used directly other than the generator coke is the carbureting oil. As the substances of which tar is composed are driven from the coal in coking, the source of water-gas tar is primarily the carbureting oil. In the water-gas process the aim is to convert as much of the oil as possible into a fixed gas with an average heating value high enough to carburet the blue gas. This conversion is never 100 per cent complete, because appreciable amounts of carbon and of condensable tarry matter always form. The latter on condensing is known as water-gas tar; it may be composed entirely of substances formed by the cracking of the oil or it may contain an appreciable amount of some of the original constituents of the oil. It is not uniform in character and quality; rather the product of one plant is frequently altogether different from that of another plant. The reason for these differences is that the operating conditions, oil used, gas standard, etc., are not the same in all plants.

The tar may be brown, thin, or watery, contain a large percentage of light oils, and have a specific gravity[1] but little greater

[1] By specific gravity is meant the density or weight of a given volume of the liquid divided by the weight of an equal volume of water.

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than 1.00; or it may be black liquid, of molasseslike consistence, containing a much smaller percentage of light oil and having a specific gravity of 1.15 or more. Again, a water-gas tar may contain little or much free carbon and naphthalene.

Obviously, in specifying tar for a particular purpose, a water-gas tar can not be either condemned or recommended unless the properties of the particular tar are known.

WATER-GAS TAR EMULSIONS.

A water-gas tar emulsion is a tar, produced as described, having in suspension small droplets of water that do not readily separate from the tar. The percentage of water that can be thus retained may be as high as 85 per cent.[2] It is not customary, however, to think of a tar as an emulsion when its water content is as low as 1 to 5 per cent.

The consistence of the emulsion depends, other things being equal, on the percentage of water dispersed in the tar. The greater the percentage of water present the more viscous the emulsion. At ordinary room temperature an emulsion containing 70 to 75 per cent water is usually thick and buttery, but one containing 2 per cent of water is approximately as fluid as a water-free tar.

The size of the droplets of dispersed water is not the same in all tar emulsions or in any particular one, but, other things being equal, the most obstinate emulsions, those having a high water content and not settling readily, contain droplets of smaller average size than the less permanent emulsions.

SOURCES OF THE WATER IN TAR EMULSIONS.

In the ordinary carbureting process the oil used to enrich the "blue gas" (generator gas) is sprayed into the hot checker chamber known as the carburetor. It should be noted that the atmosphere into which it is injected is not a *dry gas* consisting chiefly of CO and H_2, but rather a gas containing considerable moisture. The quantity of moisture present not only has an important bearing on the efficiency of oil cracking, but is of particular interest in this study. The quantities present can be approximated for any set of conditions when the true values are used in place of the assumed ones in the following:

	Cu. ft. gas.
Oil used per 1,000 cu. ft. gas made=3.2 gal	= 245
Blue gas in 1,000 cu. ft. carbureted gas	755
	1,000
Steam used per 1,000 cu. ft. carbureted gas	= 35

[2] Eighty-five per cent is not necessarily the maximum amount of water than can exist in a tar-water emulsion.

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On the assumption that the fuel is carbon the theoretical amount of steam required according to the equation[3]

$$12 \text{ lb. } C + 18 \text{ lb. } H_2O = 28 \text{ lb. } CO + 2 \text{ lb. } H_2$$

is 18 pounds of steam per 755 cubic feet of blue gas made. This is, according to the assumed values, the amount of blue gas in 1,000 cubic feet of finished gas. It is evident that, when 35 pounds of steam are used per 1,000 cubic feet of finished gas made, approximately 100 per cent more steam is used than is required theoretically. Also, as an appreciable amount of gas is made according to the equation

$$12 \text{ lb. } C + 36 \text{ lb. } H_2O = 44 \text{ lb. } CO_2 + 4 \text{ lb. } H_2$$

the actual amount of steam required to satisfy the chemical reactions in the production of 1,000 cubic feet of carbureted gas is approximately 20 pounds. Thus 35—20, or 15 pounds in excess of this amount are used.

On the assumption that one-half gallon of tar is produced per 1,000 feet of gas made—and this is not a low figure—it can readily be seen that for every volume of tar there are present in the raw gas nearly four volumes of water in the form of steam. The exact ratio[4] from the foregoing is $\frac{15}{0.5 \times 8.5} = 3.53$.

FORMATION OF EMULSIONS IN ORDINARY GAS-WORKS PRACTICE.

The temperature of the gas leaving the superheater is very high—approximately 1,200° or 1,400° F.—and is lowered rather suddenly nearly to that of the boiling point of water. Although the gas is cooled differently in different plants, in nearly all plants it is common practice to employ a water seal or wash box in the system directly after the superheater. Figure 1 shows a common form of wash box, in which the hot gas, containing tar and water vapor, is cooled considerably by direct contact with water. Although some of the tar and water condenses and are removed in the wash-box water,[5] some remains in the gas, passing to the relief holder and on through the system. As the gas is cooled the tar and water condense and, as should be expected, form an emulsion.

This emulsion does not form at only one place in the plant, but throughout the whole system to a point where the gas is free from tar. Thus the "drips" (the accumulated condensate) at the inlet and the outlet of the relief holder, scrubbers, condensers, etc., all contain tar emulsions. The tendency to form stable emulsions is not

[3] C is symbolic of carbon, H_2O of water, CO of carbon monoxide, and H_2 of hydrogen.
[4] The weight per gallon of tar in this example is 8.5.
[5] Instead of some of the water being condensed here, it frequently happens that the moisture content of the gas is increased, depending on the quantity of moisture in the gas entering the wash box and on the temperature of the gas leaving it.

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the same in the drips collected at the different places mentioned. The factors causing this difference are discussed later.

EMULSIONS IN GENERAL.

Numerous investigators, through the study of emulsions and colloidal chemistry, have disclosed some of the characteristic general properties of colloidal solutions and also some of the factors governing the rate of settling of finely divided substances held in suspension in a liquid. A large proportion of this work, however, has been devoted to the study of those emulsions in which water or water

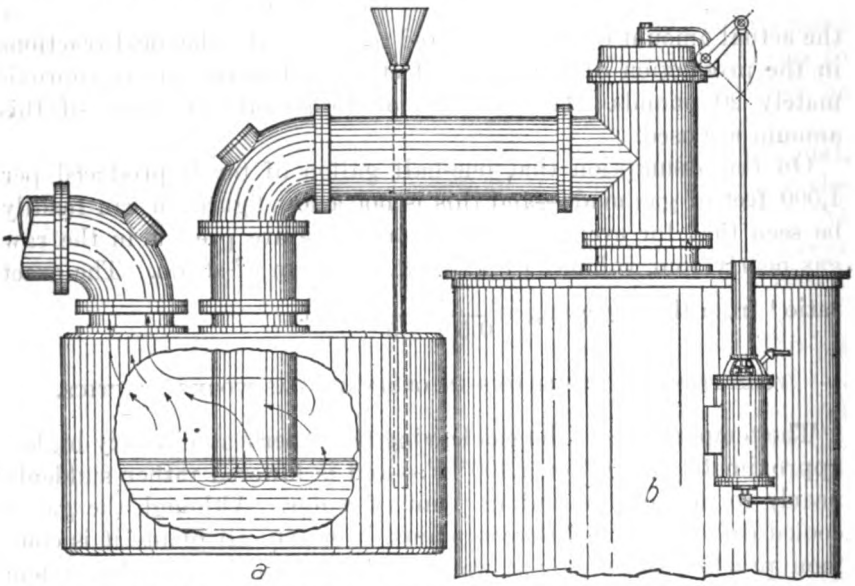

FIGURE 1.—Wash-box, diagrammatic, showing contact of hot gas with water: *a*, Wash box; *b*, upper part of the superheater.

solutions are the outer phase; that is, those in which water is the continuous medium. Water-gas tar does not tend to form this kind of an emulsion.

An emulsion is not a homogeneous system, but rather one in which minute droplets of one liquid are dispersed in another liquid. The droplets go to make up what is called the inner phase; the continuous medium in which the droplets are dispersed is known as the outer or continuous phase. The liquids composing these phases must be immiscible in one another. For the formation of the so-called permanent emulsions an emulsifying agent is also required.

Two common and different types of emulsions are recognized—namely, (1) a liquid, of the nature of oil, dispersed in water, and (2) water dispersed in an oily liquid. The type that will form depends, among other things, on the nature of the emulsifying agent.

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Arthur W. Thomas[6] states that, "in general, if the emulsifying agent is more easily wetted by water than by oil, then water will be the external phase and oil the dispersed phase; while if the emulsifier is more easily wetted by oil than by water, the reverse will be true." The writer's experiments show that this holds true for water-gas tar emulsions.

An emulsion in which water is the outer or continuous phase can be further diluted with water, but will not readily mix with additional amounts of the dispersed phase; likewise when oil (or tar) is the outer phase more oil or tar can be readily mixed with the emulsion, but not water. By this means alone it is at once evident that in a tar emulsion tar is the outer phase and water the dispersed phase.

The active agent in the formation of emulsions may be—(1) An electric charge on the dispersed particles; (2) colloids, either soluble, insoluble, or slightly soluble; (3) other substances, not strictly colloids, that may be soluble, insoluble, or partly soluble; and (4) combinations of the preceding.

Although there are many different theories regarding the mechanism of emulsions, it is common knowledge that certain substances cause one type of emulsion to form, whereas others cause the opposite type, and that the character and permanence of these emulsions depend largely on the quantity of the active agent used. Consideration must also be given to temperature, pressure, relative quantity of disperse and dispersed phase present, their specific gravities, the size of the particles of the insoluble agent, and other factors. Sodium and potassium soaps are recognized as active agents with which emulsions of oil in water can be prepared that may contain oil as the inner phase, in amounts even greater than 90 per cent. The insoluble soaps, those of calcium, magnesium, or aluminum, are active agents that cause the formation of the opposite type of emulsion, in which water is the inner phase.

The physical character of an emulsion varies as the percentage of the dispersed liquid changes, usually becoming less fluid and more viscous as the relative amount of the inner phase increases. This change is very noticeable in tar emulsions.

It is possible for an emulsion to exist when forces are present that tend to disrupt it, or rather forces that tend to create an emulsion of the reverse type. Thus in the tar-water emulsions that form in a gas works, substances are present which tend to emulsify the tar in the water, while the greater force causes the formation of the reverse type of emulsion. Usually the combination of two opposite-type emulsions in proper proportions will cause a "breakdown" or

[6] Thomas, Arthur W., A review of the literature of emulsions: Jour. Ind. Eng. Chem., vol. 12, February, 1920, pp. 177–181.

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separation of the two phases of both emulsions, but sometimes this process is slow unless means are provided, as mixing, to insure intimate contact.

QUALITY OF WATER-GAS TAR IN THE VARIOUS DRIPS OF A GAS WORKS.

The tar collecting in the storage well of a gas works is a composite representing the condensate from all the drips where tar (or emulsion) collects by condensation. If samples of the tar and water collecting in the various drips are examined, it will be found that no two of the condensates are chemically or physically identical—a result to be expected from the manner in which the gas cools. As the stability of the emulsions collecting in the various drips is not the same, one method of learning more about the factors causing the

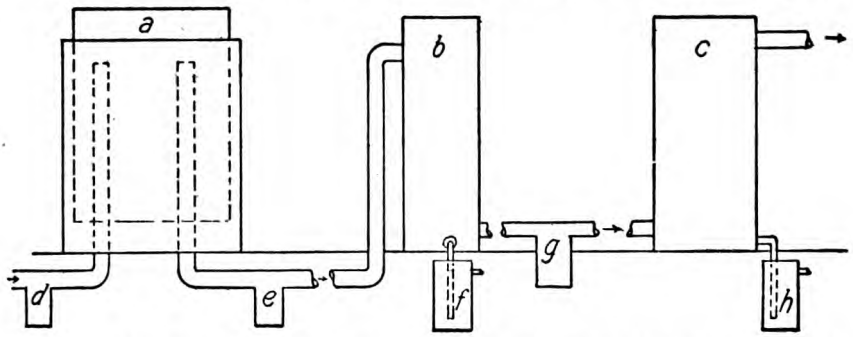

FIGURE 2.—Location of drips at which tar samples were collected: *a*, Relief holder; *b*, condenser; *c*, shaving scrubber; *d*, inlet to relief-holder drip; *e*, outlet from relief-holder drip; *f*, seal and tar drain from condensers; *g*, drip; *h*, seal and tar drain.

formation of stable emulsions is by examining the different tars collecting in the drips.

Some tar, but not a large percentage of the whole, is removed from the gas at the wash box.

In the plants chiefly considered in this paper the cooling system consisted of a relief holder and condensers. No wet scrubber was employed nor was there the customary grid scrubber directly after the wash box or at any place in the system. Some tar, however, separated at the shavings scrubber. The positions of the drips are diagrammatically shown in Figure 2.

The tar condensing nearest the water-gas set, where the temperature is highest, is more viscous, has a higher specific gravity, a higher percentage of free carbon, a higher percentage of high boiling constituents, a lower percentage of low boiling constituents, and a higher residue on distillation than the tars collecting at points further from the water-gas set, for example, at the shavings scrubber. These properties are on the basis of water free tar. The properties of the tars collecting at the various drips from the wash box to the

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shavings scrubber is progressively different as the gas is progressively cooled. This is shown to best advantage in Table 1. Since the shavings scrubber is not a condenser but removes the tar (already condensed and entrained in the gas) because of the larger contact surface exposed, it is not surprising that the properties of the tar so collected do not harmonize with the previous statement, unless allowance is made for the manner in which this tar is collected. These results were obtained at a plant where considerable difficulty was experienced with tar emulsions. It is particularly noticeable that the free carbon and paraffins (sulphonation residue) are present in the largest percentages in the tar that formed the most obstinate emulsion. Also the absence of naphthalene and other solids in the distillation fractions from this tar, is suggestive.

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TABLE 1.—*Differences in the properties of the tars collecting in the various drips of a water gas plant.*

	Inlet relief holder.			Outlet relief holder.			Condensers.			Shavings scrubber.		
Emulsion tendencies	Very strong			Weak			Very weak			None.		
Free carbon, per cent by weight	2.2			0.8			0.17			0.10.		
Specific gravity at 60° F	1.057			.938			.920			.952.		
	Per cent, by weight.	Sp. Gr. at 60° F.	Sulphonation residue, per cent, by volume.	Per cent, by weight.	Sp. Gr. at 60° F.	Sulphonation residue, per cent, by volume.	Per cent, by weight.	Sp. Gr. at 60° F.	Sulphonation residue, per cent, by volume.	Per cent, by weight.	Sp. Gr. at 60° F.	Sulphonation residue, per cent, by volume.
Distillation:												
0° to 170° C	2.0	0.911	.....	12.7	0.877	0	28.3	0.874	0	13.8	0.880	0
170° to 200° C	6.4	.928	53.0	22.9	.902	0	21.9	.907	0	29.4	.910	0
200° to 210° C				12.5	.918	0	9.7	.926	0			
210° to 235° C				26.0	.925	35.0	23.3	.939	30.0	28.8	.936	36.0
235° to 270° C	17.2	.946	64.0	11.4	.947	30.0	6.6	.958	32.0	9.1	.952	31.0
270° to 300° C	11.9	.971	62.0	1.9	.981	17.0	2.7	.989	20.0	3.4	.980	23.6
300° to 315° C	6.7	1.001	37.0									
315° to 355° C	18.9	1.038	30.0	3.9	1.033	10.0	1.4	1.062	0	2.9	1.000	10.3
Residue	35.6	Hard pitch.		7.8	Hard pitch.		4.4	Coke.	.....	8.8	Coke.	.....
Loss	1.3	.....	.....	.9	.....	.....	1.7	.....	.....	3.8	.....	.....
Total	100.0	.....	.....	100.0	.....	.....	100.0	.....	.....	100.0	.....	.....
Notes on fractions	No solids.			10 per cent solids in 235° to 270° fraction.			One-sixth of the volume of the 210° to 235° fraction was solid.			No solids.		
Sulphur in the tar, per cent	1.05			0.52			1.31			1.92.		
Total sulphonation residue of tar, per cent by volume	32.6			13.3			9.4			14.4.		

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TARS FROM DIFFERENT GAS WORKS.

Owing to the difference in operation and operating conditions prevailing in the various plants and to the differences in the raw materials used, the tar produced in one plant may be radically different from that made in another. The approximate limits between which some of the variable properties of tar may lie are given in Table 2.

TABLE 2. *Approximate limits for some of the variable properties of water-gas tar produced under different conditions. (Water-free tar basis).*

	From—	To—
Specific gravity	1.00	1.18
Fluidity	Thin fluid like oil.	Viscous heavy-bodied.
Free carbon, per cent	1.0 or less.	6.0 or more.
Distillation residue, above 355° C.,[a] per cent	40.0	70.0
Solids in distillation fractions, per cent	0.0	More than 10.
Sulphonation residue, per cent	25.0	5.0

[a] Distillation in a flask with the thermometer bulb at the offtake from the neck.

As the tars vary so widely it is not surprising that sometimes very obstinate and bothersome emulsions form, whereas at other times little, if any, trouble is experienced from them. In seeking the cause or rather some of the causes for these difficulties, we are immediately concerned with the factors affecting the quality and properties of the tar.

FACTORS AFFECTING THE QUALITY OF WATER-GAS TAR.

The factors that seem to be most important or to have the most pronounced influence on the quality of tar, are as follows:

(1) Temperatures in checker chambers.
(2) Checker spacing—(time and intimacy of contact).
(3) Rate of input of oil.
(4) Distribution of oil—(efficiency of oil spray).
(5) Kind of oil used.
(6) Average condition of checker brick (frequency of recheckering).
(7) Quantity of excess steam used.
(8) Condensing system and rate of cooling the gas.

The gas made per unit of time, the method of blasting, and numerous other variables that are not considered here also have an effect on the quality of the gas and the tar produced.

TEMPERATURE IN CHECKER CHAMBERS.

It is commonly recognized that changes of the temperature in the checker chambers have an important bearing on the quality of the gas made, as well as on the total quantity of oil consumed per 1,000

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cubic feet of gas made. It is usually conceded that if the temperature is too low, appreciably lower than 1,300° F., the oil will not be completely cracked, more of it will be required to carburet the gas, and the oil consumption per 1,000 feet of gas made will consequently be higher. Likewise it is generally known that excessively high temperatures are favorable for the formation of naphthalene and carbon. In fact, in recognition of this it frequently happens that more attention is given to the appearance of the water overflowing from the wash box than to the pyrometer readings: thus, when there seems to be free oil in this water the temperature, as recorded by the pyrometer, is increased; when the water shows indications of carbon or naphthalene the temperature in the checker chambers is lowered. This is not an accurate guide and is only helpful when consideration is given simultaneously to other variables. Expressed differently, there are other factors that affect the quality of the tar in a similar manner; that is, cause an increase or a decrease in the percentages of carbon and naphthalene in the tar. These factors are discussed in the following paragraphs; their influence on the formation and rate of settling of tar emulsions is presented under the next general heading.

The quality of tar is so readily affected by changes in the temperatures in the checker chambers that, other things being equal, the analyses of composite tar samples from a particular set could be used as a guide or check on the pyrometers.

In determining the most favorable operating temperature it is customary, among other things, to choose that temperature whereby the largest percentage of oil is cracked into gas suitable for carbureting purposes without the formation of excessive amounts of naphthalene. This temperature, in average works practice, lies between 1280° and 1400° F., the exact temperature depending on the other variables mentioned above. Now in large plants where many sets are operated at one time it is not always easy to say which set is producing an excessive amount of naphthalene, or which can be operated advantageously with higher temperatures without causing naphthalene difficulties. The analysis of the tars—composite samples from the individual sets [7]—will show which set is cracking the oil to the best advantage and which one is producing naphthalene. The kind of analysis referred to here is merely a distillation of the water free tar, wherein the specific gravity, quantity, and physical character (whether solid or liquid) of each fraction is noted, as well as the specific gravity of the composite tar. The sulphonation residue of the distillation fractions shows very closely the percentage

[7] For a method of obtaining a composite tar sample, see page 29.

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of paraffins in them and collectively indicates the relative amounts of uncracked oil in the different tars. However, the specific gravity of the corresponding distillation fractions is lower as the per cent of uncracked oil increases, and hence it is not always necessary to make the sulphonation test to determine approximately the relative oil-cracking efficiency of the different sets.

CHECKER-BRICK SPACING.

In many gas plants it is still the practice to make frequent changes in the spacing of the checkerwork in the carbureter and superheater. Frequently the "sets" in a given plant are not all checkered alike. Though the relative merits of different methods of checkering can not be considered here, attention is drawn to the fact that changes in the checkering system, brick spacing, and number of brick used not only affect the quality of the gas made but that of the tar as well. These changes, other things remaining the same, affect the linear velocity of the gas, the time of contact of the gas with the hot bricks, the intimacy of contact with the bricks, and the amount of heating surface available for oil cracking.

A prolonged time of contact at one temperature produces, in a general way, much the same cracking effect as a higher temperature with a shorter time of contact. It follows, then, that two similar water-gas sets, operated alike and with the same operating temperatures, may produce different qualities of gas and of tar if the checkering is not the same in both. It goes without saying that changes in a checkering system should be made with a definite purpose and then only after consideration has been given to the effect on other important variables. When changes of this kind are made, the analysis of the tar produced under the changed conditions might well be used as a means of arriving at the most suitable operating temperature for the prevailing conditions.

RATE OF OIL INPUT.

The rate at which oil is injected into the carbureter affects the "actual" time of contact of the oil vapors with the brick work in more than one way, and also predetermines to a considerable degree the properties of the tar formed. Some engineers advocate injecting the oil as rapidly as possible, aiming to have it all in during the early part of the run, but others favor a prolonged injection which permits only a brief purge of the set by blue gas before taking off the run. Certain disadvantages, as well as benefits, are realized from either method, and conditions may render one distinctly preferable to the other. Though the quality or the character of the tar produced

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can not be given first consideration in the choice of a method, it might to advantage be given some consideration. It is undoubtedly true that in many gas works the rate of input of the oil is not particularly considered at all.

With a slow rate of input, the oil, if effectively sprayed, will be more completely cracked and a higher gravity tar produced than when the oil is injected more rapidly.

DISTRIBUTION OF OIL.

That proper spraying of the oil, its distribution over the surface of the carburetor brickwork, is essential for efficient cracking is well known, and is only mentioned here because (1) it is an important factor affecting the quality of the gas as well as that of the tar, and sometimes receives too little attention, due perhaps to the fact that the spraying process is not visible, and (2) it has a direct bearing on emulsion difficulties.

As the oil is more uniformly and thoroughly cracked when it is injected, in a finely divided state, over the entire upper surface of the brickwork, it follows that the tar formed under these conditions contains less uncracked oil, has a higher specific gravity, and is apt to contain more naphthalene and similar solids. The last, of course, depends on the temperature of the brickwork.

KIND OF OIL USED.

With regard to gas making it is recognized that, other factors being the same, oils containing a high proportion of paraffins are preferable to those containing less. The oil-cracking efficiency on a B. t. u. basis (also considered with regard to gas making) is higher when such an oil is used and the percentage of tar formed is usually lower than with other oils. Although in the course of this investigation no tests were made to ascertain the quality of tar produced from oils of different character and grades, the writer is led to believe that when some of the heavy viscous oils are used a higher temperature is required in the checker chambers to crack them properly; and that at ordinary temperatures (those used with better oils) more oil passes into the tar and the production of tar or carbon, or of both, is increased.

AVERAGE CONDITION OF CHECKER BRICK.

After a set has been in operation for two to three weeks (sometimes less) the volume of free space between the checker bricks decreases, because of the formation of carbonaceous deposits between and on the brickwork. This may be accounted for partly by the material blown over from the generator, fuel, and ash, and in part by the

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carbonization of oil or products therefrom. Carbon from carbonization of oil tends to form over the exposed surface of the bricks a hard film, that grows thicker as the set continues in use after recheckering. As the checker work becomes clogged the linear velocity of the gas and oil vapors passing through the checker chambers becomes greater. Thus the intimacy and duration of contact are altered, and, of course, the quality of both tar and gas is affected.

Further, the physical characteristics of the surface exposed to the oil vapors are quite different as the deposit accumulates. Although it is extremely difficult to assign numerical values to the cracking propensities of different hot surfaces exposed to oil vapors, it seems clear that the surface of clean brick is preferable to that of "dirty"—that is, carbon-coated—brick. The conductivity and the specific heat of the carbonaceous accumulation are not the same as for brick. These differences all influence the quality of the tar produced.

The tar formed when the brickwork is "dirty" contains more uncracked oil—saturated hydrocarbons—less "solids" in the distillation fractions, and has a lower specific gravity. The results of analyses of tars produced under each of the conditions mentioned are presented in Table 3, which shows also how conditions influence the formation of obstinate emulsions.

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TABLE 3.—*Differences in the quality of tar produced with clean and with dirty checker brick.*

Tars from a Plant Where the Sets were in Condition for Rechecking.

	Inlet relief holder.			Outlet relief holder.			Condensers.			Shavings scrubber.		
Emulsion tendencies	Weak			Very strong			Strong			Strong.		
Settling	Readily settled to 10 per cent water when heated.			In 1 week (hot) settled to an emulsion of 60 per cent water.						Did not separate any free tar on standing 1 week.		
Free carbon. Per cent by weight	5.3			1.85			1.4			0.8.		
Specific gravity at 60° F	1.147			1.125			1.045			1.053.		
	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by volume.	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by volume.	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by volume.	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by volume.
Distillation:												
0 to 170° C	0			0			Sample lost			4.0		
170 to 200° C	2.5			0						4.5	0.939	0
200 to 210° C										3.8	.954	0
210 to 235° C	3.8	0.982	9.0	1.7	0.988					18.9	.966	18.0
235 to 270° C	10.5	1.003	12.0	7.8	1.011	14.0				16.6	1.002	29.0
270 to 300° C	7.2	1.013	14.0	7.0	1.029	11.0				4.3	1.010	9.0
300 to 315° C	5.0	1.036	17.0	4.5	1.050	(?)				3.4	1.023	8.0
315 to 355° C	15.5	1.085	6.0	14.1	1.081	1.0				11.2	1.060	0
Residue	55.4	Hard pitch.		63.5	Hard pitch.					29.0	Coke.	
Loss	1.1			1.4						4.3		
Total	100.0			100.0						100.0		
Notes on fractions that are solids at room temperature.	Solids one-half of 210° to 235° fraction; some in 300° to 315° fraction; some in 315° to 355° fraction.			No solids.						Two-thirds of 210° to 235° fraction was solid. Some solids in 315° to 355° fraction.		
Total sulphonation residue, per cent	4.9			2.8						9.5.		
Ash, per cent	.12			.22			0.15			.05.		

Oil used per run: 35 gallons in large sets; 20 gallons in small sets.

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Tars from Same Plant; Samples Collected When Checker Brick Were Clean.

Emulsion tendencies	Weak			Very weak			Weak			Very weak.		
Settling	Separated considerably on standing in the warm 2 days.			Separated to an emulsion of 7 per cent water in 2 days (warmed).			Separated slowly			Separated fairly well when warm, not in the cold.		
Free carbon, per cent, by weight	7.02			4.50			0.63			1.90.		
Specific gravity at 60° F	1.154			1.135			1.033			1.082.		
	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by vol.	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by vol.	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by vol.	Per cent, by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent, by vol.
Distillation tests:												
0° to 170° C	0	.....	0	6.6	.....	0	21.0	.....	0	6.4	.....	.....
170° to 200° C	.4	.....	0	1.7	0.908	0	9.2	0.973	0	5.8	0.963	0
200° to 210° C		.....	0	.8	.933		3.3	.....	0	3.9	.972	0
210° to 235° C	4.2	1.017	10.3	4.1	.987	0	14.6	.....	0	15.7	1.003	0
235° to 270° C	10.9	1.011	14.0	8.6	1.015	14.0	7.8	1.020	4.5	13.8	1.025	6.0
270° to 300° C	4.7	1.026	20.5	5.2	1.033	18.0	2.9	1.025	8.0	6.1	1.029	9.8
300° to 315° C	3.9	1.055	7.9	3.4	1.052	14.3	2.4	.....	8.0	2.5	1.046	3.0
315° to 355° C	16.0	1.094	3.0	10.8	1.094	0	6.3	.....	8.0	7.1	1.105	.4
Residue	57.8	Hard pitch.		57.5	Hard pitch.		28.2	Hard pitch.		36.5	Hard pitch.	
Loss	2.1	.....	.....	1.3	.....	.....	4.3	.....	.....	2.2	.....	.....
Total	100.0	.....	.....	100.0	.....	.....	100.0	.....	.....	100.0	.....	.....
Notes on fractions that are solids at room temperature.	210° to 235° fraction, four-fifths solids; 235° to 270° fraction, trace of solids; 300° to 315° fraction, one-fourth solids; 315° to 355° fraction, two-thirds solids.			200° to 210° fraction, one-third solids; 210° to 235° fraction, nearly all solids; 235° to 270° fraction, trace of solids; 270° to 315° fraction, one-fifth solids; 315° to 355° fraction, three-fifths solids.			170° to 200° fraction, one-sixth solids; 200° to 235° fraction, all solids; 235° to 270° fraction, one-fifth solids; 300° to 315° fraction, trace of solids; 315° to 355° fraction, one-third solids.			170° to 200° fraction, one-half solids; 200° to 235° fraction, nearly all solids; 235° to 270° fraction, one-fifth solids; 315° to 355° fraction, one-fourth solids.		
Total sulphonation residue	4.16			2.90			1.26			1.61.		
Ash, per cent	.54			.01			.04			.13.		

Oil used per run: 60 gallons in large sets; 25 gallons in small sets.

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QUANTITY OF EXCESS STEAM USED.

In almost all oil-cracking processes the presence of steam with the oil vapors has a marked effect on the ultimate products formed. In general, steam tends to lessen the deposit or formation of carbon. Also, it is known that, other things being equal, the efficiency of the cracking, on a B. t. u. basis, is greater in blue gas containing steam than in the dry gas. The use of a large excess of steam also causes a quicker cooling of the fuel in the generator with a resultant increase in the CO_2, carbon dioxide, content of the blue gas. The cracking of the oil into tar is not as efficient in poor blue gas as in good blue gas. These opposite tendencies may take place in greater or less degree accordingly as the quantity of excess steam is varied. The checker brick in the carburetor is cooled more quickly when a large excess of steam is used, for the specific heat of steam is considerably higher than that of blue gas. (This is true only when the gas and excess steam leave the generator at a temperature appreciably lower than the prevailing temperature in the carburetor brickwork.) Some other angles of this subject are not considered here, although they may have important bearing on the formation of tar emulsions.

Attention has already been drawn to the fact that the finished gas leaving the superheater contains a larger proportion of water than of tar. The permanency of the emulsion formed on cooling this gas depends, among other factors, on the amount of water present.

CONDENSING SYSTEM AND RATE OF COOLING THE GAS.

As the size of the water droplets in a tar emulsion has a definite influence on the stability of the emulsion, or rather on the rate of settling, it is clear that the rate of cooling and the surface contact during cooling are closely related to the emulsion problem. The actual quality of the tar that collects at any particular place in the works is similarly affected; in some places the vapors condense from the gas in a fine state of division and, at the usual velocity of the gas, are separated more completely as the amount of cooling surface is increased. In one plant the vapors condensing as a mist and at a relatively high temperature (160° F.) may be largely removed during the early stage of cooling from surface contact, whereas in another plant this condensed material may be carried along in the gas until a much later stage of cooling.

Obviously the quality of tar produced in a particular plant does not depend on a few variables, but on many. No attempt has been made to mention all these variables, but only those that seem most important. The methods of blasting, admitting air to carburetor, and making up and down runs have a bearing on the quality of tar produced, but are not considered here.

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That the factors governing the quality and character of tar should be closely related to those controlling the formation of obstinate emulsions is to be expected. Some of the latter are discussed below.

FACTORS AFFECTING THE SETTLING OF AND FORMATION OF TAR EMULSIONS.

It is natural that when gas containing tar and water is cooled more or less suddenly to a temperature below the dew point of these substances, the condensate that first collects should be an emulsion. But immediately the question arises, "Why is water always the inner phase even when present to the extent of 60 to 70 per cent of the whole?" Also, "Do all such emulsions settle or separate at the same rate, and if not, why not?" If these different effects depend wholly or chiefly on the varying composition of the tars, then the control of emulsion difficulties lies in regulating the factors affecting the quality of the tar in so far as this procedure is economical. If the effects depend on substances dissolved in the water of the emulsion, or on the size of the particles (droplets) of water, then the method of cooling the gas is of most importance. As a matter of fact, the tendency to form stable tar emulsion is affected both by the method of condensing and cooling and by the quality of the tar itself.

In one Illinois gas plant where the formation in the tar well of persistent emulsions contained approximately 73 per cent water, samples of the condensate were taken at the inlet and outlet of the relief holder, at the condensers, and at the shavings scrubber and their characteristics studied. The most obstinate emulsion was from the inlet of the relief holder, whence the tar from the shavings scrubber at the end of the cooling system separated almost instantly from the water if it formed an emulsion at all. The tars collected between these points had emulsion tendencies lying between the extremes. Now, it is known that water-gas tar contains varying amounts of so-called "free carbon"[8] which is present in a suspended state. This substance was present in greater amounts in the tars that formed the most obstinate emulsions. Inasmuch as other properties of the tar samples were different also, tests were made to show the effect of each and to find out to what extent the free carbon was the cause of the trouble.

The sample of tar from the shavings scrubber contained 0.2 per cent of carbon. When shaken with distilled water it formed an emulsion but a large proportion of it separated rapidly, the rest taking a longer time to settle. The procedure was repeated several times and the tar that settled readily was separated from the emulsion and

[8] The so-called free carbon is not pure carbon, but is a hydrocarbon of high carbon content, insoluble in benzol.

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used in the subsequent like treatment with distilled water. After a few treatments it was found that the settled tar was free from free carbon and did not show any particular tendency to form emulsions in which water was the inner phase. In fact, when shaken with a large excess of water the tar formed droplets in the water and rapidly separated as a layer on top of the water. A true emulsion was not formed. An idea of the effect free carbon has on the production of emulsions in which water is dispersed in tar, is furnished by this experiment.

Some of each sample of tar emulsion collected was put in Babcock cream bottles and centrifuged for several minutes at 1,800 to 2,000 revolutions per minute. The most obstinate or stable emulsions were not completely separated. The tar when heavier than water collected, in part, at the bottom of the bottle and some of the water separated as a clear top layer, but between these layers a zone formed, consisting of a thick buttery mass or "muck" with a very high percentage of water. The tar in this muck contained a higher percentage of free carbon than either the original sample or the tar separated in the cream bottle. A sketch of the Babcock cream bottles used appears in Figure 3. The percentage of tar separating free from water on centrifuging seems to be inversely proportional to the obstinacy of the emulsion.

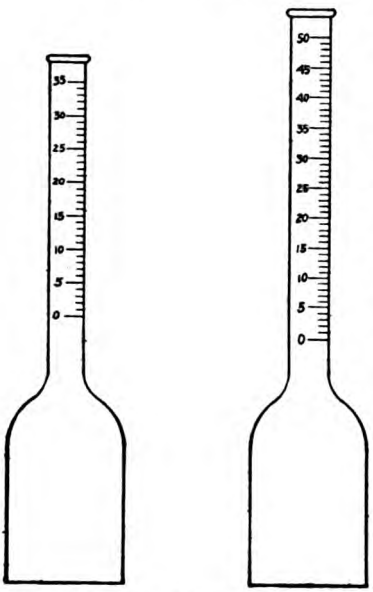

FIGURE 3.—Babcock cream bottles used for centrifuging tar emulsions.

When tar is filtered and the free carbon removed the tendency to form permanent or semipermanent emulsions is usually weak. Further evidence on the properties of carbon and its emulsifying effect is given under the heading "Synthetic tar—artificial emulsions," page 32.

During the filteration of tar another action beside the removal of carbon takes place and may bring about a separation or a partial separation of the tar and water. This action is explained in part by the opportunity offered the particles of the dispersed phase—water—to come together because of the preferential wetting of the filtering medium. The filtered and separated tar when shaken with a relatively larger amount of water forms an emulsion similar to the original if the carbon is not completely removed. Accordingly, the fineness of the mesh of the filter has considerable to do with the properties and quality of the filtered tar.

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A sample of emulsion that contained 73 per cent water and had not shown any sign of settling on standing in the laboratory at room temperature for more than a week, was squeezed through a course-mesh muslin cloth to ascertain whether any water could be separated from the emulsion in this manner. The procedure can not be called filtration, as nothing was removed from the emulsion except a small amount of large-size impurities that had no effect on the emulsion properties, but more than half of the total water present was separated so that it could be poured off as water. A thinner and smoother-looking emulsion was left that contained 55 per cent water. The procedure was repeated several times with the same

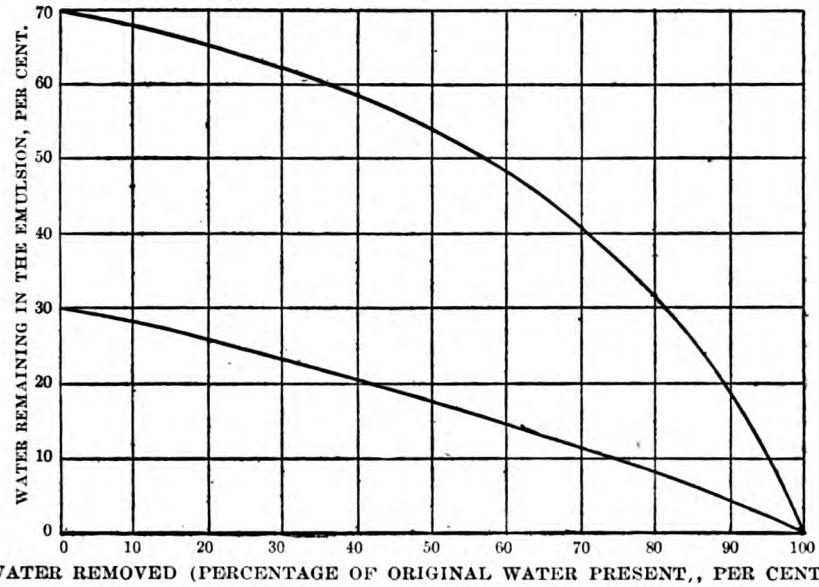

FIGURE 4.—Relation between the percentage of water removed and that remaining in the emulsion. Curves plotted are for emulsions originally containing 30 and 70 per cent water.

cloth and with a fresh cloth, but no appreciable amount of additional water could be separated. Using a cotton cloth of finer mesh reduced the water content of the emulsion, but the tar was not water free, nor did further filtrations through the cloth bring about a more complete separation. It should be noted that the cloth was wet with water at the end of the "filtration," even though in some trials it had been previously wetted with oil or tar. The water content of the emulsion after this treatment was 18 per cent. Some fine glass wool was packed to a depth of 1½ or 2 inches into a 2-inch glass cylinder against a rubber stopper at one end, fitted with a glass tube as an offtake, and the emulsion, 55 per cent water, was forced through it. The water content of the emulsion was further reduced, being

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7 per cent in the final filtered and separated product. Figure 4 shows graphically the relation between the amount of water removed and the percentage left in the remaining emulsion.

Seemingly, the fineness or the size of the droplets of the dispersed water affects the ready separation of water from emulsion by mechanical means. The rate of settling is similarly affected. Those emulsions containing water in relatively large droplets separate on standing more readily than those in which the water is more finely divided. Stokes has shown that a small sphere falling in a liquid soon assumes a constant velocity, and from the formula given for this velocity it is evident that, other things being equal, the velocity is proportional to the square of the radius. The writer does not say that water droplets dispersed in water-gas tar tend to follow this law exactly, but the indications are that the tendency to do so exists. This means that the methods of condensing and cooling employed in gas works are important in determining the rate of settling of tar emulsions.

If the raw gas is so cooled that the water condenses in an atmosphere of tarry vapor, the prospects favor the formation of an emulsion containing very finely divided water. If, on the other hand, much of the tarry matter is removed before the bulk of the water condenses, the relative concentration of the water vapor in the gas being much greater than that of the tar vapor, the water of the emulsion will be primarily in large-size droplets and will accordingly separate from the tar sooner. Emulsion difficulties, then, should practically cease if the gas was cooled more gradually and the tar removed—with a dry scrubber or some other means—before the bulk of the water condensed.

From the influence on emulsion formation of free carbon and finely divided water droplets, one might expect that the most stable emulsions would form in the condensate from the first sudden chilling of the gas after it leaves the wash box. This is exactly what happens. In the tar collecting at the inlet to the relief holder and in the relief holder, the water is most finely divided and the carbon is present in largest proportion. The exact relation of the properties of the tars collecting at various places in a plant depends on the velocity of the gas and capacity of the cooling system, as well as on the other variables.

These two factors—the free-carbon content and the fineness of division of the dispersed phase—although very important, are not the only ones to consider in dealing with emulsion difficulties. In fact, these difficulties must be overcome in spite of the presence of free carbon in the tar rather than with the elimination of it. Some of these other factors include: (1) The constituents of the tar; (2) the viscosity of the tar; (3) the specific gravity of the tar; and (4) the character of the water dispersed.

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It has already been pointed out that tars produced under different conditions, or collected from various drips at the works, differ widely in the percentages of their constituent substances. All these constituents do not behave the same toward emulsifying agents; some are more readily emulsified than others. Hence it is essential to know which can be easily emulsified and which are most resistant to the formation of permanent emulsions. This knowledge will throw considerable light on the effect of changing the variables previously listed and will signify which should be changed in order to overcome emulsion difficulties.

In order to obtain this information, tar samples were collected from two gas plants and were tested. In one of these plants emulsion difficulties were predominant; large quantities of tar congealed from the gas as an obstinate, rather permanent emulsion containing 73 per cent water. No recognizable emulsion difficulties were experienced at the other plant, which was regularly shipping tar carrying only 2 per cent of water. This difference was not due to the employment in that plant of a larger settling tank wherein tar could settle for a longer period, thus freeing itself from water.

In selecting samples it was considered unsatisfactory merely to sample the storage tanks, because of the difficulty in obtaining samples truly representative. Therefore samples were also taken at the various drips throughout the gas works, and only in plants where more than one set was in continuous operation, so that they were fairly representative of the average tars produced under the differing condition. Table 4 gives the results of these tests.

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TABLE 4.—*Results of tests made of tars, emulsions, and waters from two selected gas plants.*

Plant A.—Emulsion Difficulties Serious.

	Inlet to relief holder.			Outlet of relief holder.			Condensers.			Shavings scrubber.			Relief holder.		
Emulsion tendencies	Very strong			Weak			Very weak			None			Very strong.		
Settling properties	Separation hardly noticeable after standing 2 weeks, warm.			Slow separation when warm.			Separates readily						Practically no separation; contained 73 per cent water.		
Free carbon, per cent by weight	2.2			0.8			0.17			0.10			3.24		
Specific gravity at 60° F	1.057			0.938			0.920			0.952			1.036		
	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.
Distillation:															
0–170° C.	2.0	0.911	?	12.7	0.877	0	28.3	0.874	0	13.8	0.880	0	2.3	.....	....
170°–200° C.	6.4	.928	53.0	22.9	.902	0	21.9	.907	0	29.4	.910	0	.9	.....	....
200°–210° C.				12.5	.918	0	9.7	.926	0		.....	0	.9	.....	....
210°–235° C.				26.0	.925	35.0	23.3	.939	30.0	28.8	.936	36.0	5.2	0.920	?
235°–270° C.	17.2	.946	64.0	11.4	.947	30.0	6.6	.958	32.0	9.1	.952	31.0	17.9	.945	31.8
270°–300° C.	11.9	.971	62.0	1.9	.981	17.0	2.7	.989	20.0	3.4	.980	23.6	7.5	.983	29.8
300°–315° C.	6.7	1.001	37.0										4.0	1.010	
315°–355° C.	18.9	1.038	30.0	3.9	1.033	10.0	1.4	1.062	0.0	2.9	1.000	10.3	13.0	1.036	16.6
Residue	35.6	Hard pitch.		7.8	Hard pitch.		4.4	Coke.		8.8	Coke.		47.1	Hard pitch.	
Loss	1.3			.9			1.7			3.8			1.2		
Total	100.0			100.0			100.0			100.0			100.0		
Notes on fractions that are solids at room temperature.	No solids in the distillate fractions.			10 per cent of 235°–270° fraction was solid.			15 per cent of 210°–235° fraction was solid.			No solids.			No solids.		
Total sulphonation residue	32.6			13.3			9.4			14.4			12.0+		
Ash, per cent on ignition	.6			.07			—			—			0.57		
Sulphur in the tar, per cent	1.05			.52			1.31			1.92			—?		
Ammonia in condensed water, per cent NH_3	.007			.057			.034			.131			?		
Sulphur in condensed water, per cent	.017			.007			.01			.33			?		
Sulphocyanides in the condensed water	None.			None.			None.			Present.			.....		

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Plant B.—No Emulsion Difficulties.

Emulsion tendencies	Weak.			Very weak.			Weak.			Very weak.			Very weak.		
Settling properties	Separates readily when warm.			Separates very readily when warm.			Separates very slowly.			Separates readily when warm but not when cold.			Separates rapidly and completely.		
Free carbon, per cent by weight	7.02			4.50			0.63			1.90			3.01		
Specific gravity at 60° F	1.154			1.135			1.033			1.082			1.177		
	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.	Per cent by weight.	Specific gravity at 60° F.	Sulphonation residue, per cent by vol.
Distillation:															
0°–170° C	0.0	.....	.....	6.6	.....	....	21.0	.....	...	6.4	.....	...	1.2	0.909	....
170°–200° C	.4	.....	.....	1.7	0.908	0.0	9.2	0.973	0.0	5.8	0.963	0.0	.8	.940	?
200°–210° C				.8	.933		3.3	.....	...	3.9	.....	.0	5.0	.993	13.0
210°–235° C	4.2	1.017	10.3	4.1	.987	.0	14.6	.....	.0	15.7	1.003	.0	9.0	1.005	14.0
235°–270° C	10.9	1.011	14.0	8.6	1.015	14.0	7.8	1.020	4.5	13.8	1.025	6.0	10.0	1.018	9.0
270°–300° C	4.7	1.026	20.5	5.2	1.033	18.0	2.9	1.025	8.0	6.1	1.029	9.8	10.3	1.029	9.5
300°–315° C	3.9	1.055	7.9	3.4	1.052	14.3	2.4	.....		2.5	1.046	3.0	10.3	1.082	8.4
315°–355° C	16.0	1.094	3.0	10.8	1.094	.0	6.3	.....		7.1	1.105	.4	57.4	Hard pitch.	
Residue	57.8	Hard pitch.		57.5	Hard pitch.		28.2	Hard pitch.		36.5	Hard pitch.		2.7		
Loss	2.1			1.3			4.3			2.2					
Total	100.0			100.0			100.0			100.0			100.0		
Notes on the fractions that are solids at room temperature.	210°–235° fraction, ⅘ solids. 235°–270° fraction, trace of solids. 300°–315° fraction, ¼ solids. 315°–355° fraction, ⅔ solids.			200°–210° fraction, ⅓ solids. 210°–235° fraction, nearly all solids. 270°–315° fraction, ⅓ solids. 315°–355° fraction, ⅔ solids.			170°–210° fraction, ⅛ solids. 210°–235° fraction, all solids. 235°–270° fraction, ⅓ solids. 300°–315° fraction, trace of solids. 315°–355° fraction, ⅓ solids.			170°–200° fraction, ½ solids. 200°–235° fraction, nearly all solids. 235°–270° fracton, ⅓ solids. 315°–355° fraction, ¼ solids.			210°–235° fraction, chiefly solids. 200°–210°, 300°–315°, 235°–270° fractions contained some solids. 315°–355° fraction, largely solids.		
Total sulphonation residue	4.16			2.90			1.26			1.61			4.60		
Ash, per cent on ignition	.54			.01			.04			.13			.185		
Sulphur in the tar, per cent	1.36			1.65			.49			1.24			1.56		
Ammonia in the condensed water, per cent NH_3	.003			.007			.009			.014			?		
Sulphur in condensed water, per cent	.016			.014			.009			.014			?		
Sulphocyanides in the condensed water	None.			None.			None.			Trace.			.....		

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It will be noted that the quantity of light oils that comes over on distilling the tars up to 235° C. is appreciably less for plant A than for plant B. Also the specific gravities of the tars and of the respective distillation fractions are lower for plant A, and the tars contain less free carbon, less solids on distillation, and a greater sulphonation residue. Here again so many variables are changed at one time that a conclusion, based on the table, as to the effect of any particular change must be verified by further information. Although the factors that tend to change the quality of tar from that of plant A to that of plant B are now shown, it might be asked whether the presence of large quantities of uncracked oil in the tar has a direct bearing on the formation of emulsions or whether it is merely coincident with other changes, as in specific gravity and content of total solids, or free carbon, which have a more direct effect. A similar question may be asked about the solids present, those that chill out from the distillation fractions. Also, it is strikingly noticeable that one tar having weak emulsion tendencies has a high free-carbon content, though the presence of free carbon is recognized as a cause of the formation of emulsions. This exception suggests that either the other properties, which change simultaneously as the free-carbon content increases, have a greater influence than free carbon on the formation of emulsions or that the emulsifying effect of free carbon increases with an increase in the amount present in tar up to an optimum point beyond which further increments do not increase proportionally the emulsion tendencies. These questions are considered and discussed under the heading "Synthetic tar—artificial emulsions" (p. 32).

The table shows, however, that, regardless of which change is a cause for the formation of emulsions and which is coincidental with other changes and does not affect emulsion tendencies, the more completely the oil is cracked the less the trouble from emulsion. This is true in spite of the fact that both the viscosity and the free-carbon content may increase as the cracking is more complete.

Other things being equal, an increase in viscosity will decrease the rate of settling of suspended matter. It is desirable, therefore, that the tar be as thin and fluid as possible in order that settling may be quicker. As the most favorable tar to make, all variables being considered simultaneously, is one with high viscosity, it follows it is desirable to reduce the viscosity of the tar (in the form of emulsion in the settling well) by heating it and thus facilitate settling. Water and tar separate much more rapidly from a hot emulsion than from a cold one.

It has often been said that the cause of tar and water emulsions can be ascribed to the specific gravity of the tar being near that of water. This is not the case, although in general it is true that in

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the presence of emulsifying agents the tars with specific gravities nearest to 1.00 emulsify more readily than those of higher specific gravity, and that the tendency is for the droplets to exist in a finer state of division. Also the rate of settling when once an emulsion is formed depends on the specific gravity of the tar, and, other things being equal, the settling rate is more rapid as the difference between the specific gravities of the water and tar is increased. Thus it is evident, although tars with gravities close to 1.00 tend to form the most obstinate emulsions, that cause of the formation of emulsions can not be ascribed to specific gravity. If the tar had exactly the same density as the water at a particular temperature, then, of course, the tendency for the gravitational separation of the two phases would be nil at that temperature, and the chief cause for the resulting obstinate emulsion might be ascribed to the specific gravity of the tar. This condition does not arise ordinarily in gas-works practice, although attention is here called to what the writer saw in one plant.

A large percentage of the total tar from the various plant drips was pumped into the relief holder, which was used as a storage tank, and a persistent emulsion, 73 per cent water, formed that settled very slowly. Investigation showed that the specific gravity of the tar congealing on the inlet side of the relief holder was 1.03, and that of the tar from the holder outlet drip was 0.95. After allowance is made for the difference in quantity of each of these tars it appears that the tar condensing in the relief holder must have had a specific gravity of approximately 1.00. This is the most unfavorable condition for settling. The tars collected from other parts of the works had a low specific gravity and would of themselves separate, on standing, into tar and water, but when pumped with heavier tar (from inlet to relief holder) into the relief holder, the resultant complex mixture would not readily separate into tar and water, which is not surprising.

The character of the water, or rather the water solution, condensing with the tar has some bearing on the emulsifying tendencies of a tar, as is to be expected. From the known properties of certain solutes the determination of the substances in the water should aid an understanding of the rôle of the latter in the formation or separation of tar emulsions. As shown in Table 4, the water from the various dips was tested for total sulphur (as sulphur in solution), free ammonia, cyanides, sulphocyanides, etc. Tests of surface tension alone would perhaps have shown the relative effects or properties of the various waters tested, but the obtaining of the additional data was considered desirable. It was not possible, however, in the time allowed, to make complete and quantitatively accurate analyses

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of these waters for tar acids and other substances that may have been present in small quantities.

Ammonia, soda, or potash soaps dissolved in water so lowers the surface tension of the water that a large percentage of oil can be emulsified in the water, water being the outer phase. On the other hand, the insoluble (in water) soaps of the heavier metals can form the opposite kind of an emulsion, with oil as the outer phase, like tars. When one type of emulsion is mixed with the other in proper proportions the emulsion tends to separate into water and oil. It follows that if any of the waters carry a similar colloid or other substance capable of causing the formation of emulsions in which water is the outer phase, the tendency for the tar to emulsify will in part be neutralized. Ammonia sulphur compounds—the polysulphides—and the sulphocyanides of ammonia, it appears, promote the formation of this type of emulsion, and, therefore, when present in the water condensing with the tar they tend to retard the formation of tar-water emulsions. If the normal tendency of the tar to emulsify is weak, the presence of these compounds in the associated water causes a rapid and complete settling. A certain shaving-scrubber tar separated quickly from the water condensing with it, but when shaken with distilled water in a flask it formed a more permanent emulsion. Ammonia phenol compounds probably would act in the same way, although an appreciable amount of tar acids is not ordinarily present in either the tar or the water.

Sometimes the drip water is cloudy from finely divided sulphur. This sulphur seems to have the property of affecting surface tension and emulsification tendencies in the same way as the ammonia compounds mentioned. Competent investigators, studying the properties of sulphur and other colloids have concluded that colloidal sulphur does not have a decided effect in causing emulsification, hence it may be that the property here ascribed to colloidal sulphur may be accounted for by adsorbed ions or by causes not due to sulphur as such. These tests were not so complete as to warrant contradicting the findings of others.

OPERATING WITHOUT EMULSION DIFFICULTIES.

From the foregoing it may be concluded that by following a particular and definite procedure in operating, the emulsion difficulties experienced in some plants can be largely, if not entirely, overcome. This can be done if plant conditions are such as to permit employing the desired method and changes. The important details and essentials of operation are presented here as follows:

1. It is essential that the temperature in the checker chambers should be kept high enough to crack the oil as completely as pos-

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sible; in fact it might be said without material misstatement that, with other things in proper adjustment, the temperature should be high enough to crack the carbureting oil completely. It should be remembered that pyrometers frequently require checking or adjustment and that different grades of oil require different temperatures to crack completely under given conditions. An analysis of the tar produced by any particular set will give the desired information on the efficiency of oil cracking, which may be used as a rough check on the pyrometer readings. It is not necessary that the tar tested should be a representative sample of the total tar produced by a particular set, but rather it seems sufficient to sample the tar condensing and separating from the gas before it reaches the main containing the gas from numerous sets. Of course, the results of tests are more comparable and more accurate when uniform samples of tar are collected in laboratory apparatus by condensing and scrubbing a portion of the gas entering the inlet to the wash box. When a number of sets are operated simultaneously, it is possible that one or more of them may be producing an inferior tar[9] that depreciates the value of the total tar produced. In adjusting conditions the importance of such test is evident.

Pyrometers do not always tell the whole story. For example, it is usually assumed that the temperature at the base of the carburetor is the same as at the lower portion of the superheater and that a pyrometer end (thermocouple) in the lower end of the superheater is a sufficient guide for the temperature control of the set. Some operators carry this a step further and use a pyrometer recording the temperature in the upper part of the superheater only. In this instance it is easy to operate with a relatively cold carburetor and a hot superheater with the resultant insufficient cracking of the oil and trouble from tar emulsions.

The method of blasting the carburetor has considerable to do with the relative temperature of the two checker chambers. Overblasting during the early stage of the blast period, a common practice in some plants, is one cause of a relatively low temperature in the carburetor. The generator blast gas is not rich during the early stage of blasting, and it frequently happens that instead of the carburetor air being throttled at this stage and increased in steps during the blasting, the air valve is opened wide as soon as the generator blast is started. As a result the mixture of lean gas and excess of air absorb heat from the top courses of the carburetor brickwork during the early stage of the blasting, combustion not

[9] By inferior tar in this instance is meant tar containing a large percentage of uncracked oil and readily forming rather permanent emulsions with a high content of water.

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taking place until the mixture is heated enough. The rate of flame propagation may be too low at this stage for combustion to be carried back from the superheater or the bottom of the carburetor. Under some conditions, however, excess of air is beneficial, for it supports combustion of a part of the carbon deposited on the lower brickwork of the carburetor.

2. During a run the oil should not be admitted faster than it can be thoroughly cracked. The oil-spray nozzle should be tested with oil, and at the same pressure as when in operation, to make sure that proper distribution and the desired spray effect are obtained. A pressure gauge should be used in this test, because it often happens that spray nozzles are tested with city water at 80-pounds pressure per square inch, that being considered the approximate pressure at the spray nozzle during the period of oil input, whereas the actual pressure found by the writer in numerous plants where these tests were made is rather commonly between 5 and 18 pounds per square inch, averaging 10 pounds, and not 70 to 80 pounds, as supposed.

3. More oil can be thoroughly cracked when the checker brick are clean than when they are "dirty"—coated with carbon and ash dust, etc.—other things being the same. The effect of "dirt" is decided and can be readily checked by analyzing at intervals the tar produced from the time the clean brick are put in place until the set is shut down for recheckering. It is essential that the brickwork be kept clean and changed frequently enough to eliminate this factor tending to cause the formation of permanent tar emulsions. Obviously, the exact number of operating hours that can be safely obtained under all conditions can not be stated. In plants operating over a part of each 24-hour day there is a period wherein the carbon, or at least much of it, can be burned out of the checker chambers. Under these conditions the brickwork will not need changing as often as when operation is continuous. Again, the blast pressure has considerable bearing on this point, for with high blast pressure more material is blown over from the generator. A figure that is used by some gas companies operating sets continuously is to use the brick for 1,000 operating hours (approximately six weeks' continuous operation) before changing them. It is necessary that the checker brick be changed often enough to permit efficient cracking of the oil if trouble from tar emulsions is to be avoided.

4. In some gas plants the checker brick is placed in flue formation, as shown in Figure 5, rather than in staggered formation, as shown in Figure 6. While much can be said about checkering, and from many different viewpoints, it seems clear that when emulsion difficulties prevail the bricks should not be placed in flue forma-

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tion. The intimacy of contact is impaired and usually not as efficient oil cracking can be obtained as with staggered formation.

5. Too sudden cooling of the gas is to be avoided. An ideal arrangement would be cooling the gas in stages and removing the material condensing above the dew point of the water in the gas

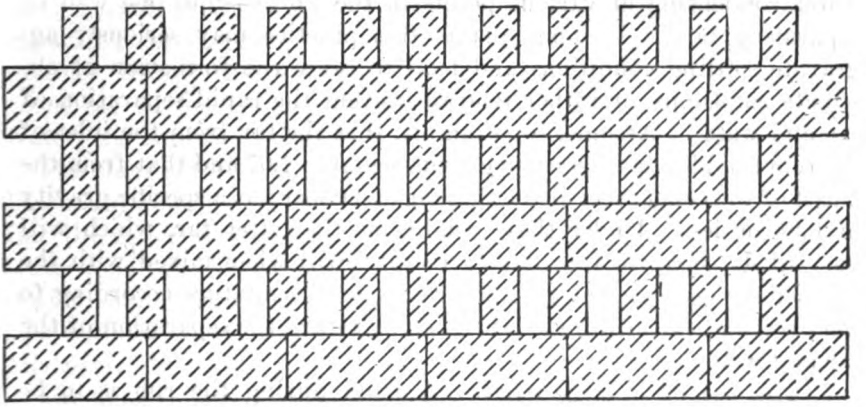

FIGURE 5.—Showing checker brick arranged in flue formation.

before this water condenses. Such an arrangement is hardly practicable in the apparatus as now built. However, the principle might well be utilized as far as possible.

It is advisable, the writer believes, to use a dry grid scrubber in the cooling system following the wash box. The present tendency

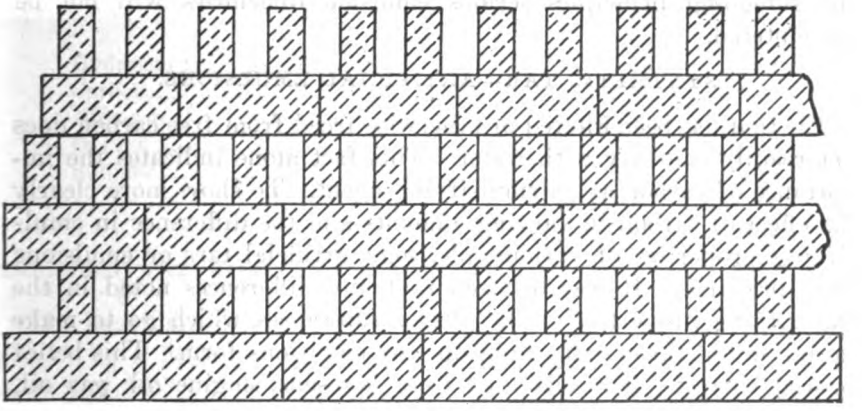

FIGURE 6.—Showing checker brick arranged in staggered formation.

is away from this practice, because it causes more back pressure on the set during the run. As to retarding the formation of emulsions, the scrubber is of benefit in causing a separation from the gas of much of the condensed tar in suspension which can thereby be largely removed before much of the water condenses. Hence a

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dry scrubber properly placed in the cooling system should be a benefit in those plants where conditions favor the formation of tar emulsions. This, however, is not a statement of proved fact but is an opinion based on theoretical considerations.

6. It is almost universal practice to pump the drips—the tar and water condensing at various points in the works—into one well or separating tank. In some plants this practice may seriously aggravate settling conditions and tend to cause the formation of obstinate emulsions, or rather tend to prevent the rapid separation of tar and water. Assume, for example, that the tar from the inlet of the relief holder has a specific gravity equal to 1.07 and that from the outlet of the condensers or the shavings scrubber has a specific gravity of 0.98 or less. Under these conditions the latter tar, which will very likely separate from water readily, will when mixed with the heavier tar decrease the specific gravity of the mixture according to the percentage of it present, and thereby retard the separation of the tar and water.

7. The use of a large excess of steam during the run is to be avoided, not because more water will condense with the tar, but rather because of the effect on the temperature of the carburetor brickwork and of other effects. For best efficiency only so much steam should be used as is necessary; hence reference is made here to the use of excess steam merely because it is not given full consideration in some plants.

The writer firmly believes that when close attention is given to the foregoing principles serious emulsion difficulties will not be encountered.

SYNTHETIC TAR—ARTIFICIAL EMULSIONS.

Tar that has been filtered or otherwise freed from free carbon does not readily emulsify with water. This fact alone indicates the importance of carbon as an emulsifying agent. To show more clearly the effect of carbon in varying amounts and the difference in emulsifying properties of various oils, some artificial tars or emulsions were prepared. It was believed that any differences noted in the emulsifying properties of the oils or substances which go to make up tar would throw some light on why emulsions form. This belief proved correct. The oils used were kerosene, engine oil, gas oil, the various tar fractions as collected during the tests, and motor fuel made from the oil obtained by stripping gas.

The emulsions were prepared by adding weighed amounts of carbon to the oil or to a mixture of oil and water in a glass-stoppered 100-c. c. graduated cylinder, diluting to a mark that gave the desired percentage of each ingredient, and shaking in a definite manner a given number of times.

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When the oils were separately shaken with water only, percentage of water being in excess of 50 per cent by volume, no emulsions formed, or rather the emulsions that formed separated rapidly into layers of oil and water. On shaking the light shavings-scrubber tar (A in Table 4) with distilled water, the volume of water being 70 per cent of the whole, a rather poor emulsion formed, which separated on standing. When the same tar was treated in like manner, except that the ammoniacal water (originally separating from tar at the shavings scrubber) was used instead of distilled water, the emulsion separated much more quickly and was coarse.

The chief solid materials used for making emulsions were carbon black and alumina. The former was apparently a very fine powder, but the latter was not as fine as desired and when agitated with water separated very quickly, the faintly cloudy liquid showing that only a small amount remained in suspension. When shaken in the oils without water, the carbon separated on standing and left the oils perfectly clear.

The analysis of the carbon black was as follows:

Analyses of carbon black.

	Samples as received.	Moisture-free sample.
Moisture	2.34	0.00
Volatile matter	6.16	6.31
Fixed carbon	91.50	93.69
Ash	.00	.00
	100.00	100.00
Hydrogen	.78	.53
Carbon	92.90	95.13
Nitrogen	.08	.08
Oxygen	6.22	4.24
Sulphur	.02	.02
	100.00	100.00

EMULSIONS WITH GAS-OIL DISTILLATION FRACTIONS AND WITH KEROSENE.

The heavy fraction and the largest fraction obtained by distilling gas oil in a flask in the same manner as tar distilled over between 315° and 355° C. It was agitated with distilled water and the resulting temporary emulsion separated completely within a few minutes. With water in large excess, water was the outer phase; with oil in excess, oil was the outer phase. Perhaps a true emulsion was not formed under these two conditions.

Small amounts of carbon black materially changed the character of a similarly prepared mix. When 70 c.c. of water were mixed with 30 c.c. of the same oil and with 0.3 gram of carbon black and

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agitated in the same manner, a moderately viscous emulsion was produced that had the appearance and physical properties of an obstinate tar emulsion. Water was the inner phase and no water separated after the emulsion had stood several days. This emulsion was as resistant to centrifuging as the obstinate tar emulsions. Although water was present as the dispersed phase to the extent of 70 per cent by volume, only 0.3 per cent by weight of carbon was required to hold the emulsion. After the emulsion had stood several days 2 c.c. of the oil (2 per cent of the emulsion) separated as a layer on top. When this experiment was repeated with 1 per cent of carbon black, instead of 0.3 per cent, it was found that the emulsion formed was much thicker—more viscous—that no oil or water was released from the emulsion after standing several days. This product showed no tendency to separate even after standing a week at room temperature. Some of the characteristics and properties of the oil used as well as the oil from which it was obtained by distillation are shown as follows:

TABLE 5.—*Analysis of gas oil.*

Distillation fraction.	Per cent by weight.	Specific gravity of fractions at 60° F. (15.6° C.).	Sulphonation residue, per cent.
0 to 210° C.	0.0	.....	.....
210 to 235° C.	1.8	.....	.....
235 to 270° C.	7.4	0.831	93
270 to 300° C.	14.2	.841	92
300 to 315° C.	5.9	.849	90
315 to 355° C.	62.2	.865	71
Residue	4.4	.....	(Viscous oil.)
Loss	4.1	.....	.....
	100.0	.....	.....

Although the specific gravity of the oil used to prepare this emulsion was only 0.865, as shown in the table, nevertheless separation did not take place. It should be noted that this oil was chiefly a paraffin oil—containing 71 per cent of paraffins—and that it was rather viscous at room temperature.

Similar attempts were made to prepare emulsions with kerosene oil. This oil behaved much the same as the distillation fraction above, a small amount of carbon sufficing to hold 70 per cent of water (dispersed) in a very stable emulsion. None of the water separated from the emulsion on standing several days at room temperature although somewhat more carbon was required to hold all the oil in the emulsion. Attention is drawn to the fact that kerosene oil is not as viscous as the distillation fraction from gas oil used in the previous experiment. The kerosene oil had a spe-

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cific gravity of 0.814 at 60° F. and gave a sulphonation residue of 92 per cent by volume.

EMULSIONS FROM TAR OILS, MOTOR FUEL, ETC.

From the numerous tar distillations made during the course of these experiments composite samples were collected representing the different fractions as distilled, and these oils were used to make emulsions with carbon black and water as above. A mixture of 70 c.c. of water and 30 c.c. of the composite sample, 0° to 170° C., was vigorously shaken in a graduated cylinder; on standing a few minutes the water and oil separated completely. This was repeated with the addition of a trace of carbon black. An emulsion formed in which water was the dispersed phase, but the emulsion was coarse and separated very rapidly. The droplets of water appeared to be very large and the carbon seemed to form a film around them. With more carbon black added the emulsions produced became finer and more permanent; in fact, 0.3 gram of carbon black was sufficient to hold all the water, though most of the oil separated on top as a clear layer apparently free from carbon black. The oil had a specific gravity of 0.875 at 60° F., and was not viscous. This oil was not so readily held in emulsion as the oils containing a high percentage of paraffin oils.

The heavier distillation fractions of tar are still less easily held in emulsion. Thus when 70 c. c. of water was mixed with 30 c. c. of the naphthalene fraction (composite oil) distilling between 210° and 235° C., it required 2 grams of carbon black to hold the water as a stable emulsion. This oil was saturated with naphthalene at the prevailing room temperature; it was not so fluid as the 0° to 170° C. fraction, but was not viscous; its specific gravity was 0.9447 at 60° F. Although the specific gravity of this oil is much nearer unity than that of the other oils thus far mentioned and the oil is thicker than the 0° to 170° fraction, the oil strongly resists emulsification in spite of the fact that the sulphonation residue was 28 per cent.

The heavier fraction, the one distilling between 315° and 355° C. (composite sample) shows difference in emulsifying properties. This oil is viscous at room temperature and is heavier than water. When shaken with water—equal parts by volume, and without carbon black—an emulsion formed with water as the inner phase. This emulsion was thick and viscous but separated on standing. When a larger percentage of water was used, up to 75 per cent of the whole, the oil formed droplets in the water and separated rather rapidly on standing. In emulsions containing carbon black to the extent of 2 per cent of the whole, some water separated and 60 per cent water was the most that could be retained, under the conditions, for one

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hour. This oil had a specific gravity of 1.06 and a sulphonation residue of less than 2 per cent.

These heavy tar oils that contain naphthalene, anthracene, and their compounds seem to have the power of resisting the formation of emulsions, whereas the paraffin oils readily tend to form stable emulsions. By using small amounts of carbon black in mixtures of tar oils and paraffin oils emulsions can be prepared by simple shaking that can not be distinguished by appearance, from the natural tar emulsion, and are as stable.

Motor fuel, consisting chiefly of benzol and toluol, was mixed with water in the same proportions as above (70 per cent water and 30 per cent oil) and made into emulsions by adding definite proportions of carbon black and shaking. The purpose was to ascertain what amount of carbon black was most favorable to the formation of stable emulsions, and to note the effect of the addition of quantities greater than the optimum amount. The results of these experiments are given in Table 6.

TABLE 6.—*Effect of different amounts of carbon black on the formation of stable emulsions of motor fuel and water.*

No.	Volume of water used, c. c.	Volume of oil used, c. c.	Total volume, c. c.	Weight of carbon black used, grams.	Carbon black.		Character of emulsion formed.
					Per cent of total.	Per cent based on oil present.	
1	70	30	100	0.15	0.15	0.6	Very weak; unstable. Large droplets of water.
2	70	30	100	.60	.62	2.3	Weak. Droplets of dispersed water smaller than in 1.
3	70	30	100	1.50	1.53	5.7	Fair. Thin fluid.
4	70	30	100	3.00	3.02	11.3	Fair. Water droplets small. Fairly stable.
5	70	30	100	3.60	3.60	13.6	More viscous than in 4. Water separated. Optimum passed.
6	70	30	100	4.20	4.17	15.9	More viscous than in 5. Additional amount of water separated.
7	70	30	100	5.10	5.02	19.3	Very thick. Much water separated.
8	70	30	100	6.00	5.86	22.7	Pasty mass. Most of the water separated.
9	70	30	100	7.50	7.21	28.4	Puttylike mass. Practically all the water separated instantly.

As the amount of carbon was increased to 5.7 per cent of the oil used, the droplets of water seemed to become smaller and the emulsion was more stable. Seemingly, there is an optimum amount of carbon that should be used to prepare the most stable emulsion; for this particular oil the amount is between 5.7 and 12 per cent of the oil used. For paraffin oils the amount of carbon required to make stable emulsions is less and the optimum amount of carbon is considerably smaller.

Since the free carbon in tar appears to act much like carbon black in emulsifying properties, one can easily understand why coal tar

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containing 20 per cent or more of free carbon does not form emulsions. The free carbon content is, of course, not the only reason for the difference in this respect between the two kinds of tar. Also a good guess might be made as to why emulsions invariably form when coal gas and water gas are mixed previous to cooling and purifying.

In the early stage of this study it was not clear how the free carbon could account for the stability of water-gas tar emulsions, when operation at high temperatures yields tars with a higher percentage of free carbon and with little tendency to emulsify. This fact is explainable by the difference in specific gravity of the tars, the differences (in properties and in percentage present) of the constituent paraffin oils, naphthalene, etc., and also by the fact that large proportions of carbon do not increase the emulsifying properties beyond that caused by small proportions. It should be noted that the percentage of free carbon required to form the most stable emulsion is not necessarily as high as the proportion of carbon black required. The writer believes that the optimum amount of free carbon for the formation of stable water-gas tar emulsions is not more than 4 per cent. The fineness of division, as well as the physical properties of the so-called "carbons" used, have considerable bearing on the proportions required to form stable emulsions. This is clearly brought out by employing powdered coal of different degrees of fineness and carbon black, mixing them separately in different proportions with a tar emulsion, and noting the rate at which water is expelled from the emulsion; or by making emulsions with uniformly varied quantities of these materials and noting the properties of the emulsions formed. When bituminous coal powdered to pass through a 60-mesh sieve and mostly of a size between 60 and 100 mesh was mixed with a water-gas tar emulsion containing 78 per cent water, the weight of coal required to eliminate all the water from the emulsion was 125 per cent of the weight of the tar, whereas when carbon black was used the weight of it required was only 40 per cent of the dry tar. The optimum quantity of any particular "carbon" is not the same for all oils or tars.

Other variables may alter the value of the optimum quantity of carbon for forming emulsions, even for a given oil and a given carbon. For example, water-soluble substances that change either the acidity, alkalinity, specific gravity, viscosity, surface tension, etc., effect emulsification. Attention has been drawn to the fact that sodium or ammonium soaps in water solution tend to form emulsions in which water is the outer phase, whereas the "insoluble soaps," lime soaps, etc., and alumina tend to form emulsions in which water is the inner phase. A soda soap so lowers the surface tension of water

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that a small amount of it is capable of emulsifying large amounts of oil in water. Examination of the water condensing from the gas along with the tar revealed no substance that had a great effect on emulsification. However, appreciable amounts of ammonia, sulphur, and ammonium-sulphur compounds are present in some of the water that condenses from the gas. These substances do affect the formation of stable tar emulsions, and their influence, though not so strong as that of carbon, is of the opposite sign. In other words, these compounds exert a force tending to form emulsions of a type the reverse of those formed by the properties of carbon. The ammonia and sulphur compounds are not present in appreciable quantities in the tar water that condenses during the early stage of cooling the gas, but rather in the last water to condense. The tar emulsion condensing with this water has low stability. Although water is the inner phase, because of the carbon present in small amounts, the emulsion is of a different form. When shaken with distilled water, however, this tar forms a fairly stable emulsion.

Alumina (Al_2O_3)[10] is mentioned here not only because it has some properties of opposite sign to that of carbon, but because these properties may have a bearing on the separation of tar emulsions, particularly those emulsions in which the tar has a specific gravity lower than water. When a mixture of oil, water, and levigated alumina is thoroughly agitated, an emulsion forms in which water is the outer phase. A mixture composed of alumina, 3 grams; oil (paraffin oil),[11] 70 c. c.; water, 30 c. c., gives a viscous buttery emulsion. It is noteworthy that the dispersed phase is oil instead of water, which is present to the extent of nearly 70 per cent and that only a small amount of alumina was required to produce this condition.

SURFACE-TENSION TESTS.

In order to show further the relative ease with which the different oils and distillate fractions of tar could be emulsified, a number of surface-tension tests were made. The surface tension of water in oil was determined by the drop method, the same apparatus being used throughout the tests. No great degree of accuracy is claimed for these results and they are given here merely to show the approximate relative behavior of the different oils. These values are given in Table 7 and not being expressed in dynes or other standard units, can be used only to show a relation.

[10] Alumina is only one of a number of materials having properties that tend to cause emulsification of oils.

[11] The oil used in this experiment was the 315° to 355° C. fraction obtained by distilling gas oil.

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TABLE 7.—*Relative values for the surface tension of water in oils, and also the specific gravity and sulphonation residue of the various oils.*

Oil used.	Surface tension of distilled water in oil, relative values.	Sulphonation residue of the oil, per cent by volume.	Specific gravity of oil.
Kerosene	25.3	92.0	0.8140
Kerosene+2 per cent crude naphthalene	20.0	90.0	.8180
Kerosene+7 per cent crude naphthalene	17.6	85.5	.8225
Kerosene+12 per cent crude naphthalene	14.8	81.0	.8300
Kerosene+15 per cent crude naphthalene	14.0	78.2	.8320
Kerosene+20 per cent crude naphthalene	15.1	73.6	.8380
Naphthalene fraction (210° to 235° C.), composite sample; clear oil freed from suspended solid naphthalene	9.6	28	.9447
Kerosene+naphthalene fraction 50/50	10.0	60	.8861
75 per cent kerosene by volume	12.8	69	.8696
25 per cent composite anthracene fraction			
Light engine oil	19.2	84	.8917
Gas-oil fraction, 315° to 355° C.	13.0	71	.8620
Composite tar fraction, 0° to 170° C.	12.4	0	.8750
Anthracene-oil fraction, 315° to 355° C.	(1)	(2)	.....

[1] Not clear at room temperature; not tested.

[2] Less than 2 per cent.

The surface tension of water in the paraffin oils is shown to be greater than that of the tar oils; that of water in the naphthalene fraction is the lowest recorded in the table. The anthracene-oil fraction, collected from 315° to 355° C., would probably show an even stronger effect than the latter. It was a thick sirupy liquid containing less than 2 per cent of paraffins, but it was not clear at room temperature. It was not tested other than in mixtures with kerosene, and its effect in one mixture is shown in the table.

Similar experiments were made using, in place of distilled water, dilute solutions of tar acids, phenol, ammonium polysulphide, colloidal sulphur, and the waters collected with the various samples of tar. The oils used in this series of tests were the composite sample (0° to 170° C.) from the distillation of tar and the fraction (315° to 355° C.) from the distillation of gas oil. Ammonia and phenol slightly lowered the surface tension of water in oil; the polysulphides of ammonia lowered it considerably, and colloidal sulphur reduced it decidedly. In fact, water condensing with tar at the shavings scrubber was cloudy after filtration, apparently from colloidal particles, and had a surface tension (in the composite 0° to 170° C. tar distillate) of 5.6 as compared with 12.4 for pure distilled water in the same oil. A lowering of the surface tension of water is unfavorable to the formation of stable emulsions, and it is evident that the water condensing with tar contains nothing that could aid the emulsification of water in tar.

METHODS OF SEPARATING WATER FROM EMULSIFIED TAR.

In the average gas plant the method of separating the tar from the water is simple; the tar emulsion is pumped into a tank and allowed to stand until it separates. The beneficial action of heat is

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recognized, and in some plants attempts are made to heat the emulsion. Again, it is not uncommon practice to pump the tar emulsion into the relief holder and in this manner keep it warm until separation is nearly complete. Where the storage tank is not large enough to allow time for separation to take place before shipment, emulsion troubles become a regular and continuous source of annoyance. If, however, the storage tank is relatively large and the tar is kept rather hot no trouble from emulsions and "slow settling tar" may be experienced for some time after the formation of obstinate emulsions has begun. Then the trouble, when it appears, may seem of more recent origin than it actually is. Thus some plants have emulsion troubles periodically, and it becomes necessary to empty the well or tanks and to give away, burn, or otherwise get rid of the emulsion.

Numerous methods, including various modifications of distillation, heating in thin layers in a vacuum, centrifuging, etc., have been suggested for dehydrating tars. Most of the methods that have been suggested are more or less costly and unsatisfactory. Although this investigation did not include methods of separating the tar and water of emulsions, some of the factors involved were necessarily considered and therefore a few of the "possibilities" in developing a separation process are mentioned here.

FILTERING THROUGH A SCREEN.

Perhaps the most simple treatment of a tar emulsion is forcing it through a screen, or a coarse cloth, of such mesh that the free carbon will not be removed in the process. Some emulsions, particularly those of high water content, after being forced through the screen will separate into a layer of water and a layer of emulsion in which the percentage of water is much lower than in the original emulsion. The amount of water removed depends on the fineness of mesh of the filter. The finer the mesh the lower will be the water content of the filtered product, the limit of fineness being the point where the screen becomes clogged with the free carbon removed. Other mediums, such as mineral wool, glass wool, or similar materials, will answer on a laboratory scale as well as a screen or cloth.

AMALGAMS.

Another way in which water can be expelled from tar emulsion, and completely so, is by mixing finely powdered coal with them until the tar has all been "taken up" by the coal (absorbed and adsorbed) as in the experiments with carbon black. The tar remains in a putty-like mass, amalgam, which may be burned direct or thinned with additional water-free tar and used for fuel or for purposes other than those for which tar is commonly used. There are numerous

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patents covering the manufacture and use of prepared liquid fuels; those of recent date bear more particularly on this use of tar.[12] Experimental work has been done and is now under way by a number of investigators looking to the utilization of liquid colloidal fuels and amalgams for the manufacture of combustible gas, and for the production of coke with the recovery of special by-products.[13]

These and other special uses for such materials may make this method of dehydrating tar, or rather of utilizing the tar of emulsions, seem more promising and profitable.

USE OF ALUMINA OR SIMILAR SUBSTANCES.

When alumina in a fine state of division—a fine powder—is mixed with oil it facilitates the formation of an emulsion of oil in water. The force exerted is of the opposite sign to that of free carbon or lampblack, as already shown, and it would, therefore, seem possible to add enough alumina or similar substance to a tar emulsion to neutralize the effect of the carbon and thus cause a separation of water. This can be done, but as the water present is finely divided the emulsion must be thoroughly mixed with the substance in order to approach complete separation. The use of alumina or a similar substance might prove a feasible method for treating tars lighter than water; as alumina is heavier than water, is wetted by water, and separates at the bottom with the water, there would be practically no contamination of the tar by it.

MISCELLANEOUS METHODS.

Theoretically the addition of a large excess of the dispersed phase—water in tar emulsions—should bring about a separation. In tar emulsions separation does not happen when a moderate excess of water is used with some agitation or mixing. A tendency to separate, however, undoubtedly exists, and this idea or its equivalent has been made the subject of a patent. C. A. Klein[14], in his process, forces the tar through a screen into warm water (over 40° C. 104° F.) to accomplish separation. Again, he causes a jet of steam to impinge on a jet of tar emulsion over water.

In the skimming process, or continuous distillation with the removal of water and light oils, dehydration is accomplished, but the process is not convenient for small plants.

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[12] Bates, L. W., Liquid fuel, Canadian patent 204,260, Sept. 28, 1920; Liquid fuel, Canadian patent 204,267, Sept. 28, 1920; Fuel, Canadian patent 204,259, Sept. 28, 1920; Atomizable fuel, British patent 149,306, Dec. 22, 1919. Jolte, W., Solid fuel—Fuel mixture—U. S. patent 1.285,208, November, 1919. Dalton, Richard F., Fuel composition, Canadian patent 189,256, Mar. 25, 1919; Artificial fuel, U. S. patent 1,260,286. Hughes, C. M. C., and Lovell, R. G., Fuel, British patent 127,024, Mar. 17, 1917. Tinker, F. T., Fuel oil, British patent 132.960, Dec. 24, 1918. See also Power Plant Eng., vol. 25, Jan. 1, 1921, p. 62, and Reports of Submarine Defense Assn. of New York.

[13] Bates, L. W., Producing gas, process. Canadian patent 206,182, Dec. 7, 1920.

[14] Klein, C. A., British patent 131,087, Apr. 26, 1918.

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Another method that has been proposed is distillation under pressure in a still provided with a release valve. The frothy tar that passes out through this valve is further heated in a superheater, the tar separating and the water and some light oil passing to a condenser.

SUMMARY AND CONCLUSIONS.

Although the time allowed for the conduct of this investigation was limited to a few months, the writer feels that his conclusions, which are in the main presented here in summarized form, are justified and are true:

1. In present systems of cooling carbureted water gas and condensing the liquid products therefrom, it is natural that emulsions of some sort, stable or weak, should form in the normal operation of a gas works.

2. The stability of the emulsions formed increases as the completeness of oil cracking decreases.

3. The relative completeness of oil cracking in different sets in a particular plant can be determined by testing the tars.

4. The free carbon of the tar is the emulsifying agent that causes the formation of emulsions in which water is the dispersed phase.

5. The obstinacy or stability of emulsions is not the same for all tars containing the same percentage of free carbon. Expressed differently, the emulsifying effect of carbon is not the same for each of the oil constituents of water-gas tar.

6. *Other factors being practically the same*, the tendency to form stable emulsions, through the presence of a definite amount of carbon, is greater as the percentage of uncracked oil in the tar increases. By uncracked oil is meant the oil that appears as a clear oil residue when the distillate oil from tar is sulphonated.

7. In ordinary operation the most stable emulsions are formed of those tars which contain the largest percentage of saturated oils. Thus the chemical composition of the tar has considerable to do with the rate of separation of the tar emulsions. A change of chemical properties is, of course, accompanied by a change in physical properties.

8. Naphthalene, naphthalene compounds, and other unsaturated high-boiling compounds of like nature obtained by distilling water-gas tar, are not as readily held in stable emulsions containing a high percentage of water, by the presence of free carbon, as are the paraffin oils.

9. In the ordinary operation of a gas works the factors that tend to increase the completeness of oil cracking also tend to increase the percentage of naphthalene and of high-boiling oils of

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the tar, increase the specific gravity of the tar, increase the percentage of free carbon, and decrease the percentage of paraffin oils in the tar.

10. Although tars with a specific gravity approximating 1.0 tend more readily to form stable emulsions with water, it is evident that a low specific gravity merely indicates a relatively high content of paraffins or indicates other chemical difficulties that cause the formation of obstinate emulsions, and is in itself not a primary contributing cause of emulsion troubles.

11. There is an optimum proportion of carbon favorable to the formation of stable emulsions carrying a high proportion of water. This optimum percentage is not the same for all oils and tars.

12. When carbon black, powdered coal, or the like is mixed with tar (or tar oils) and water, in proportions higher than the optimum there is a distinct tendency for the agglomeration and separation of the dispersed phase (water). If the proportion of the material added is large enough, the separation of water is practically complete. In this instance the tar and carbonaceous material exist as an amalgam in the form of a puttylike mass.

13. The quantity of carbon or carbonaceous material necessary to expel completely the water depends primarily but not wholly on its fineness of division.

14. The amalgam may be utilized as a paste fuel or a liquid fuel by adding to it enough dry tar or other liquid fuel to give the desired fluidity.

15. The factors (viscosity, temperature, etc.) that affect the formation and the rate of settling of tar emulsions have been discussed.

16. The primary causes for incomplete cracking of oil in the production of carbureted water gas seem to be as follows:

(*a*) Low temperature in the checker chambers.

(*b*) Dirty (carbon-coated) checker brick.

(*c*) Insufficient time of contact of the oil vapors with the hot checker brick, which may be due to injecting the oil too rapidly, to the method of checkering, or to the style of set in use.

(*d*) Changing the kind and quality of oil used without altering other variables to suit the new condition.

(*e*) Unsuitable spray nozzle. One not adjusted to give the proper distribution of oil under the prevailing conditions of pressure and rate of oil input.

17. Methods of making the various tests and analyses, or references to them, have been given.

18. A rapid and inexpensive method for the determination of water in tar emulsions has been developed. It is discussed in the appendix.

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APPENDIX.

RAPID METHOD FOR THE DETERMINATION OF WATER IN TAR EMULSIONS.

INTRODUCTORY NOTE.

Two simple and rapid methods for determining the water content of tar emulsions were employed during the course of the experiments described. These methods are presented here in the belief that they will be of interest to the gas industry.

It is frequently desirable or necessary to know how completely the emulsion has separated in the storage tank, particularly when a shipment is to be made, and the distillation method commonly employed is often time-consuming and tedious. Sometimes during a distillation test the tar "spits"; that is, a portion of it blows over into the distillate retainer, and then the test is spoiled or the results are not accurate. In testing tars for water content, it is not always necessary to know with absolute accuracy how much water is present, and determinations accurate to 1 per cent of the total sample usually suffice unless the samples represent shipment lots.

PREVIOUS WORK ON THIS DETERMINATION.

Aside from the various modifications of the distillation methods, only two methods seem to have been used for determining water in tar. Brunkow [1] evaporated a heavy oil-gas tar, containing no light oils, in a drying oven, and Kayser [2] has described a calcium carbide method. The former is evidently of limited application; the latter, though probably accurate, is difficult to perform and requires elaborate apparatus.

The standard method of determining the water in tar is, of course, by distillation. In the method of the Barrett Co., as described by Weiss,[3] 200 c. c. of the emulsion are mixed with 200 c. c. of light oils and distilled to 400° F., the water being collected and measured. An accuracy of 0.1 per cent is claimed. In view of the sources of error inherent in the method, such as water sticking to the sides of

[1] Brunkow, Herbert E., Tar from California oil gas. Gas Age, vol. 38, Sept. 15, 1916, p. 280.

[2] Proceedings Pacific Coast Gas Ass'n, vol. 8, 1910, p. 468.

[3] Weiss, J. M., Methods of analysis in the coal-tar industry. I—Crude tars: Jour. Ind. Eng. Chem., vol. 10, September, 1918, pp. 734–738.

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the condenser and the solubility of water in the oils, a limit even of 0.1 per cent seems very small; if the mixture shows any considerable tendency to "spit" (froth and boil over) the limit will be much higher. A determination by this method requires considerable time and attention, as well as much desk space.

There is, however, another method, which, so far as the writer is aware, has not been used for tar, but has been much used for the analogous petroleum emulsions. It is common practice to determine water in those by adding a light gasoline and centrifuging the mixture; the water goes to the bottom and its volume can be read directly.[4] This method is the same in principle as Method I described below.

METHOD I.—CENTRIFUGING WITH A HEAVY SOLVENT.

This matter makes use of the fact that tar emulsions can be mixed with heavy solvents. The tar is completely dissolved in the solvent, so that the water droplets are suspended in a liquid that is much heavier than water and much thinner than tar; then, by centrifuging, it is not difficult to bring all of the water to the surface where its volume can be easily measured.

Apparatus for carrying out this method can be obtained ready-made, as apparatus used for testing milk and cream is quite suitable. The author used an ordinary hand centrifuge made for milk testing, one built to accommodate eight bottles at one time; with it a speed of about 2,000 r. p. m. could be attained.

The bottle used is shown in Figure 3; it holds about 50 c. c. and has a long slender graduated neck. The graduations are numbered, each unit representing 0.2 c. c.

The qualities most desired in the solvent fluid used are high specific gravity, low viscosity, a good solvent for tar, and immiscible with water; also the higher its surface tension the better, other things being equal. Carbon tetrachloride and carbon bisulphide, of common liquids, best fulfill these conditions. The latter was found to be slightly the better; but its ready inflammability and disagreeable odor led to the preference of carbon tetrachloride.

Most tars, however, when mixed with the solvent and centrifuged for a reasonable time in a hand centrifuge, do not seem at first sight to separate from water completely. The upper part of the neck of the bottle contains clear water, and the body contains solvent with tar dissolved in it. Between these, but having no sharp upper boundary, is a dark and rather thick material somewhat

[4] Allen, I. C., and Jacobs, W. A., Methods for the determination of water in petroleum and its products. Tech. Paper 25, Bureau of Mines, 1912. Gives an excellent review, with references, of all the methods proposed for determining water in petroleum emulsions.

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like the original emulsion. It varies in amount with different tars, being generally most abundant with the most obstinate emulsions, when it may occupy more room than the clear water.

Closer inspection, however, shows that this material is lighter colored than the tar solution below, and has a sharp lower boundary. If a glass rod be inserted in the bottle, practically all of this material can be drawn out, sticking to the rod. If it is then rubbed on glass, the water in it separates and the bulk of the remainder, mainly carbon, is very small. In other words, the whole part of the liquid above the sharp line between the tar solution and the sludge may be considered, without any great error, as being all water. If greater accuracy is desired, a longer centrifuging will reduce this sludge still further, and even cause its elimination.

Seen from above, the water and carbon bisulphide surface and the water and carbon tetrachloride surface are convex. In the centrifuge, however, such surfaces are flattened, so that the line of demarcation on the neck of the cream bottle represents a flat surface of contact, for the stain will remain even when the meniscus changes shape—if the sludge permits a change of shape. It is, therefore, necessary to allow for this in reading the upper surface by choosing a point intermediate between the upper and lower edges of the meniscus.

The method as carried out is as follows: Weigh out 10 grams of tar emulsion into a cream bottle. Fill the bottle nearly to the neck with carbon tetrachloride and mix well by shaking carefully. Fill the bottle to the top graduation with carbon tetrachloride and centrifuge. Two to three minutes at 2,000 r. p. m. are ample for most determinations. Read the number of divisions occupied by the water, counting all the sludge as water, and taking as the upper mark a point halfway between the top and bottom of the upper meniscus. Twice the number of divisions equals the percentage of water by weight. If percentage by volume is desired, take 10 c. c. of emulsion instead of 10 grams.

The cream bottles can be obtained with necks of different diameters. During the course of this study use was made of bottles of 30, 35, and 50 divisions, according to the amount of water in the tar.

In some experiments made with a synthetic tar emulsion prepared from anhydrous tar, carbon, and water it was found that the results seemed slightly high, but the differences were within the necessary errors in reading the volume of water. For large amounts of water (say, 75 per cent) the method is accurate within the limit of 1 per cent. The smaller the amount of water in the emulsion the more accurate is the method.

Evidently this method is more rapid than the distillation method; two determinations can easily be made in less time than would be

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required to set up the apparatus for a determination by distillation. Eight determinations can be made and the apparatus cleaned in half an hour.

METHOD 2.—SEPARATION BY MEANS OF CARBON BLACK.

Method 2 depends on the fact that carbon black has a strong absorption power for the tar oils. Carbon black is a light, fluffy powder somewhat similar to lampblack, and is made by the imperfect combustion of natural gas. When it is added to an oil or tar, in proportions determined by the character of the oil, it forms a pasty mass having the consistence of heavy putty; for tar the amount required is about one-fifth the weight of the tar. This tendency is so strong that when carbon black is added to a tar emulsion it will draw the tar, as it were, away from its network around the water, leaving the water drops free to unite and be poured off.

The method of making a determination is simple. Weigh out into a mortar 100 grams of the emulsion. Add successive small portions of carbon black, mixing well with the pestle, until the residue becomes a thick paste like thick putty; pour off into a graduate the water that separates from time to time. Knead the paste well with a spatula or pestle until no more water separates. The cubic centimeters of water separating represent directly the percentage of water in the original emulsion.

Evidently the accuracy of this method is greater the larger the amount of water present, for the chief source of error is the water retained in the paste. It was found that this loss could be represented very well by adding to the water found 2 per cent of the percentage of anhydrous tar. With this correction, the results obtained were close to the true value. Not enough work was done to determine whether the factor, 2 per cent, is suitable for all kinds of tar emulsions; probably each analyst can determine this factor for his particular use. For emulsions of high water content the correction is obviously not of much importance.

DISCUSSION OF THE METHODS.

APPLICABILITY.

The distillation method works easily and quickly for tars low in water, but becomes tedious for tars containing much water and is sometimes difficult. Method 1, though suitable for all percentages of water, is most satisfactory for emulsions low in water content. Method 2, on the contrary, is best suited for emulsions of high water content.

COST OF MATERIALS.

The cost of materials is small for all three methods, and in comparison with other factors need not be considered.

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APPARATUS NEEDED.

Method 2 has the advantage, as its requirements for apparatus and materials are few. Method 1, on the other hand, requires a centrifuge and special glassware. The distillation method is intermediate.

TIME.

The two methods here proposed are far quicker than the distillation method.

ACCURACY.

A carefully conducted distillation should have the advantage. Which of the other two methods is the better depends on the water content of the tar.

CONCLUSION.

It seems probable that for the sale of tar and tar emulsion the methods here proposed can hardly compete with the distillation method, especially as the latter is quite firmly entrenched in contracts. For routine works analyses, however, where the highest accuracy is not required, these methods will, it is thought, be found very useful, as they require, especially method 2, only a small fraction of the time of a distillation. Many laboratories may not find it profitable to invest in a centrifuge, but a can of carbon black costs little and may save much time and trouble.

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